

SPECTRAL RESPONSES OF ELECTRODEPOSITED CUPROUS OXIDE THIN FILM ELECTRODES

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Abstract: Photoresponse of the electrodeposited cuprous oxide thin film electrodes were investigated in a photoelectrochemical cell. Spectral response measurements reveal that a Schottky-type junction is formed at the junction between the substrate and cuprous oxide resulting in n-type and p-type photosignals in a photoelectrochemical cell. The electrodeposited cuprous oxide is an n-type semiconductor.

Key words: Cuprous oxide, electrodeposition, photoelectrochemistry, photoresponse.

INTRODUCTION

Cuprous oxide is an inexpensive and non-toxic semiconductor with the potential for use in low-cost solar energy converting devices.¹⁻⁴ Understanding the control of the different semiconducting properties of cuprous oxide will facilitate progress in this field. Cuprous oxide thin films prepared by electrochemical methods produce n-type photosignals in photoelectrochemical cells, irrespective of the well established p-type conductivity.⁵⁻¹⁰ Various interpretations have been made to explain this behaviour.⁷⁻¹⁰ We present here the results of spectral response measurements of electrodeposited cuprous oxide thin film electrodes in order to establish the conductivity type of this material.

METHODS AND MATERIALS

Thin cuprous oxide films were deposited on copper and platinum and also on tin oxide coated glass substrates by the previously reported method of electrodeposition.⁶ Electrodeposition was carried out under galvanostatic current density of 10 mA/cm², in an aqueous electrolyte containing 0.3 M cupric acetate and a platinum wire as the counter electrode. The temperature of the electrolyte was maintained at 80°C and it was stirred continuously using a magnetic stirrer. Photoresponse of the film electrodes were measured in a three electrode electrochemical cell containing an aqueous solution of 0.1M sodium acetate. The counter electrode was a platinum wire and the reference electrode was a mercury sulphate electrode (MSE). Electrolytic solutions were prepared using Millipore HQ deionized water and reagent grade chemicals. They were deoxygenated in the electrochemical cell by argon bubbling during the experiments.

The spectral response measurements of the photoelectrodes were made using the phase sensitive detection method to monitor the photocurrent signal produced by a chopped monochromatic light beam. An apparatus consisting of a monochromator (Jobin Yvon H 20), potentiostat (PAR 273 A), a lock-in amplifier

(EG,& G Brookdeal 5208) and a mechanical chopper was used. The chopping frequency was 23 Hz.

RESULTS

The typical current-potential behaviour, obtained under chopped white light illumination, for a cuprous oxide film coated on a tin oxide electrode is shown in Figure 1. Similar results were obtained with cuprous oxide films coated on copper and platinum substrates. The photoresponse, shown in Figure 1, is anodic (n-type) in the potential range of about - 0.6 to - 0.3 V vs MSE and is cathodic (p-type) for more cathodic potentials. It was observed that cuprous oxide films were stable in the 0.1 M sodium acetate electrolyte in the potential domain studied here and the results were reproducible. Similar results have been reported earlier on the electrodeposited cuprous-oxide thin films on various substrates and also on cuprous oxide films formed on copper electrodes when they were exposed to aqueous electrolytes.⁵⁻¹⁰

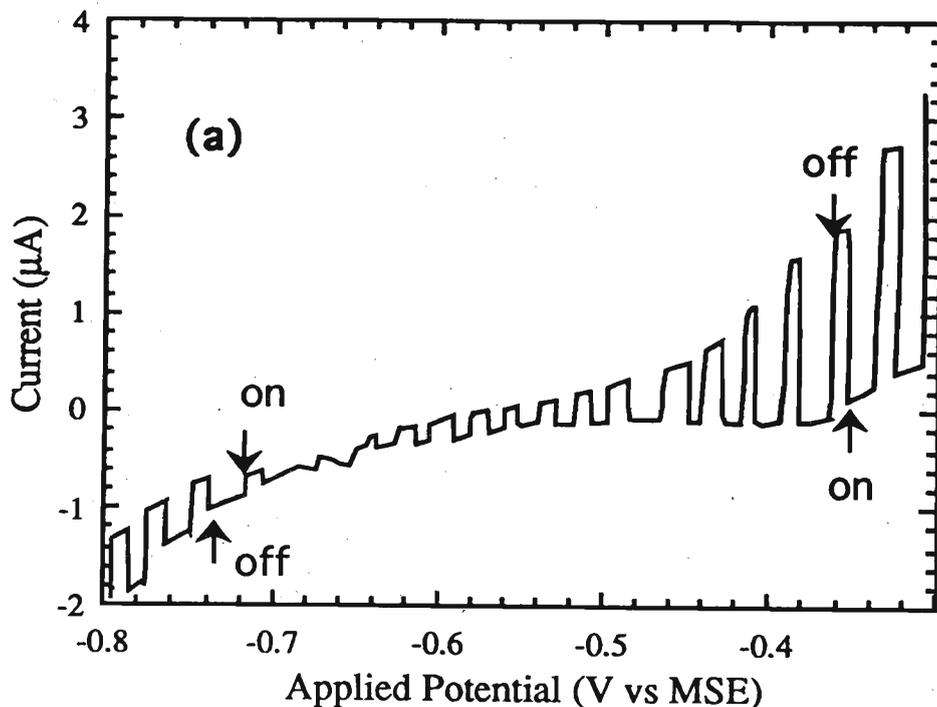


Figure 1: Current - potential variation for a thin cuprous oxide film, on a tin oxide coated glass substrate, in 0.1 M sodium acetate solution under chopped white light front illumination.

In general, anodic or cathodic photosignals are associated with the potential distributions at the semiconductor/electrolyte interfaces and are predominantly determined by the electrical conductivity type of the semiconductors. For a

sufficiently thick space-charge layer, the photogenerated majority carriers resulting in the space charge layer are driven away from the junction producing the corresponding photosignal in the external circuit. In general, as the thickness of the space charge layer is varied by the applied potential on the electrode, the magnitude of the photosignal varies. For longer wavelengths, where the absorption depth is higher, the change in the photosignal with the potential is very significant. This can be used to study the potential distribution at the semiconductor/electrolyte interface. In our study here, we used tin oxide coated glass as the substrate to electrodeposit thin cuprous oxide films because then the electrodes can be illuminated from both directions. Namely, electrodes can be illuminated either through the electrolyte (front illumination) or through the substrate (back illumination). In this way, it is possible to study the space charge layer from both directions.

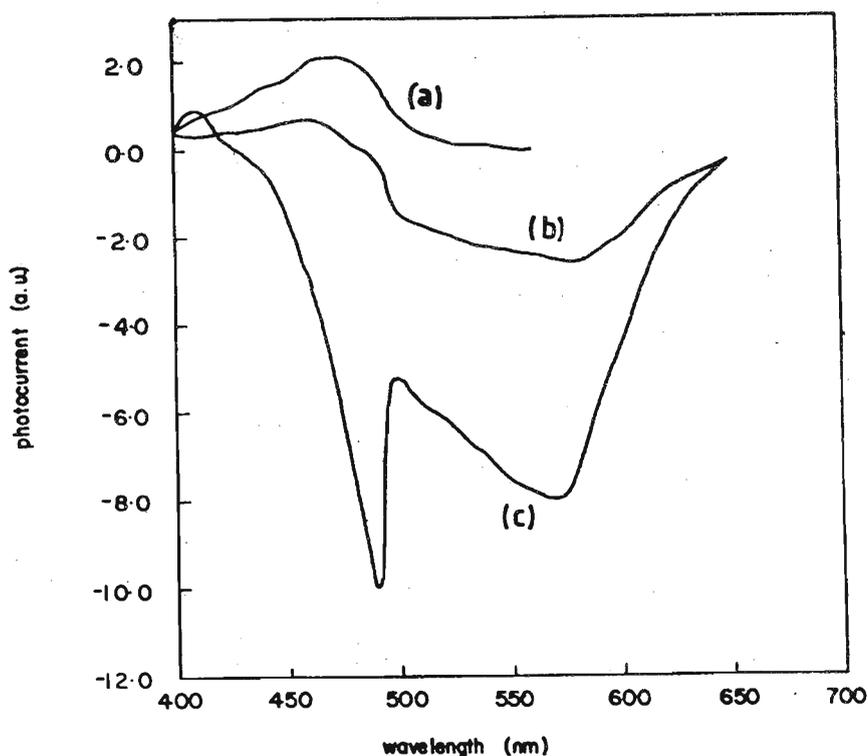


Figure 2: Photocurrent spectrum of cuprous oxide thin film on tin oxide substrate (front illumination) at the applied potential (a) - 0.3 V vs MSE (b) - 0.5 V vs MSE (c) - 0.8 V vs MSE. The spectra are not corrected for the lamp spectral distribution.

The current-potential variation of the cuprous oxide film electrode prepared on a tin oxide coated glass substrate, shown in Figure 1, was obtained under front illumination. Figure 2 shows the photocurrent spectra for the same electrode at three electrode potentials: (a) - 0.3 V vs MSE (b) - 0.5 V vs MSE (c) - 0.8 V vs MSE.

It is clear that the spectral response changes from anodic to cathodic as the electrode potential is varied from anodic to cathodic, which is in very good agreement with Figure 1. However, most interestingly, the spectral response at more anodic potential is limited only to shorter wavelengths, Figure 2(a), whereas, more pronounced photoresponse at longer wavelengths is observed at cathodic potentials, Figure 2(c). Figure 3 shows the photocurrent spectra for the same electrode obtained under back illumination leaving other conditions similar to those in Figure 2. It is clearly seen in Figure 3(a) that if the electrode is biased anodically, the spectral response is cathodic for shorter wavelengths and anodic for longer wavelengths. However, if the electrode is biased cathodically, Figures 3 (b) and (c), the spectra become cathodic.

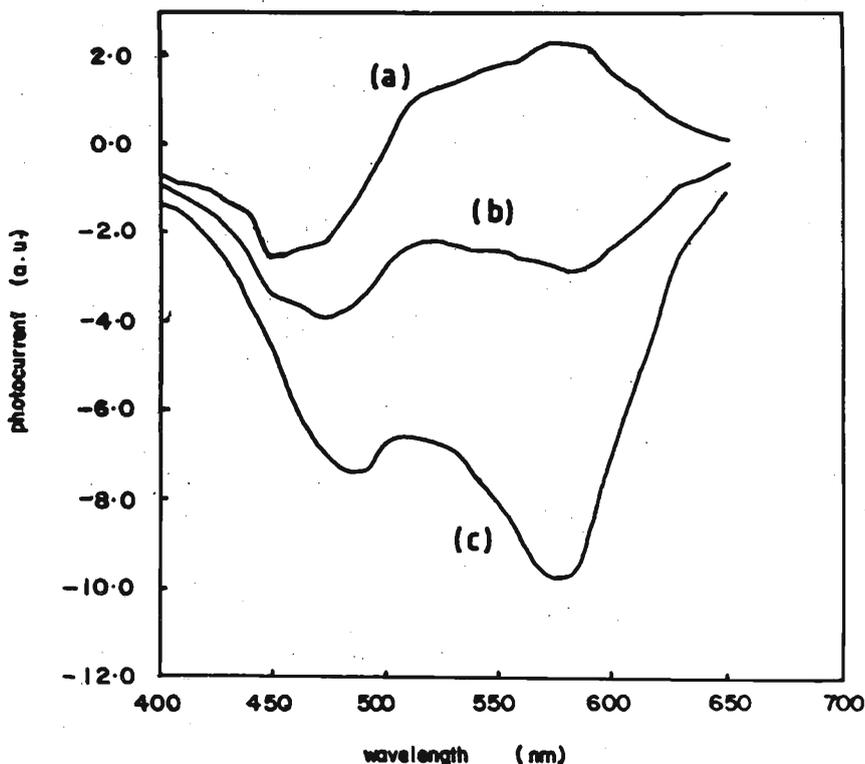


Figure 3: Photocurrent spectrum of cuprous oxide thin film on tin oxide substrate (back illumination) at the applied potential (a) -0.3 V vs MSE (b) -0.5 V vs MSE (c) -0.8 V vs MSE. The spectra are not corrected for the lamp spectral distribution.

DISCUSSION

It is evident that the separation of photogenerated carriers produced by shorter wavelengths, which absorb more closer to the cuprous oxide/electrolyte interface, becomes more efficient at anodic potentials and that the direction of the current flow is n-type. If the electrode is biased cathodically, on the other hand, the separation of the photogenerated carriers produced by the longer wavelengths

becomes more efficient and the direction of current flow is p-type. Since at anodic potential the photocurrent for shorter wavelengths is n-type, the barrier potential at the cuprous oxide/electrolyte interface is an n-type Schottky barrier. Similarly, one could expect that there exists another space charge layer at the tin oxide/cuprous oxide interface, where it could provide better charge separation for longer wavelengths. At cathodic potentials this space charge layer must be able to produce p-type photosignals and, therefore, must also be able to drift the photogenerated electrons towards the cuprous oxide / electrolyte junction. This is possible if the junction at the back contact is n-type. The existence of two space charge layers could be further established by the results, where the spectral responses were taken under back illumination. The spectral response at the anodic potentials is p-type for shorter wavelengths and n-type for longer wavelengths. Thus, at anodic potentials there exist two space charge layers and they drive photogenerated carriers in opposite directions. If the electrode is biased cathodically, the entire spectrum becomes p-type, and then the space charge layer at back contact becomes dominant. Thus in general, the n- and p-type nature of the spectral response is determined by the two contributions coming from photogenerated carriers resulting from the two space charge layers *viz.* the magnitude and the direction of the photocurrents, which determine whether the signal is n-type or p-type, are determined by the wavelength of the light and the thickness of the space charge layers. Since the general behaviour of the photoresponse is true for all the substrates studied here, the above interpretation is valid for electrodeposited films prepared on copper and platinum, as well. Further, our observation supports the idea that the electrodeposited cuprous oxide is an n-type semiconductor.

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